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(54) **Softening through the wash compositions**

(57) The present invention relates to detergent compositions comprising a clay softening system and specific selected brighteners.

EP 0 753 567 A1

DescriptionField of Invention

5 The present invention relates to detergent compositions containing a clay softening system. More in particular, the present invention relates to softening through the wash detergent compositions comprising a clay softening system and selected brighteners.

Background of the Invention

10 Detergent compositions providing fabric softening through the wash cycle have been described in art. In particular, clays are well known as fabric softening agents through the wash. The relative ability of the softening clays to meet various performance criteria is very much depending on the presence and concentration of adjunct detergent ingredients.

15 One of the types of adjunct detergent ingredients that is added to detergent compositions are dye transfer inhibiting polymers. Said polymers are added to detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto other fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

20 Polymers have been used within detergent compositions to inhibit dye transfer. Examples of such polymers are vinylpyrrolidone polymers such as described EP-A-265 257 and EP 508 034. Unfortunately, said vinylpyrrolidone polymers tend to interact with the clays formulated therewith. Accordingly, both the dye transfer inhibiting performance of the polymers and the softening performance of the clays are negatively affected.

It has now been found that specific selected brighteners are very compatible with clays in that the dye transfer inhibiting performance of the brighteners is not negatively affected in the presence of clays. In addition, it has been found that the softening performance of clays formulated with the specific brighteners has been maintained.

25 This finding allows us to formulate detergent compositions which have both excellent dye transfer inhibiting properties and softening performance.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

30 This finding allows us to formulate detergent compositions which have both excellent softening and brightener performance.

Summary of the Invention

35 The present invention relates to detergent compositions comprising a clay softening system and specific selected brighteners.

Detailed description of the invention

The compositions of the present invention comprise as an essential element a clay softening system :

40 The clay softening system comprises a fabric softening clay and may additionally comprise a clay flocculating agent.

The fabric softening clay

45 The clay softening system hereof will comprise a fabric softening clay present in an amount of at least 0.5%, preferable from 4% to 30% by weight of the dye transfer inhibiting composition. The preferred clays are of the smectite type. Smectite type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq/100g.

50 Smectite clays can be described as three-layer expandable materials, consisting of alumino-silicates or magnesium silicates.

There are two distinct classes of smectite-type clays: in the first, aluminium oxide is present in the silicate crystal lattice, in the second class of smectites, magnesium oxide is present in the silicate crystal lattice.

55 The general formulas of these smectites are $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ and $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$, for the aluminium and magnesium oxide type clay, respectively. The range of the water of hydration can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na^+ , Ca^{2+} , as well as H^+ can be co-present in the water of hydration to provide electrical neutrality.

It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can

become involved in equilibrium exchange reactions with cations present in aqueous solutions. In such equilibrium reactions, one equivalent weight of solution cation replaces an equivalent of sodium, for example, and it is customary to measure clay cation exchange capacity in terms of milliequivalents per 100g. of clay (meq/100g.).

The cation exchange capacity of clays can be measured in several ways, including electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as set forth in Grimshaw, The Chemistry and Physics of Clays, Interscience Publishers, Inc. pp. 264-265(1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ionexchange capacity somewhere in the lower portion of the range, ca. 26 meq/100 g. for an average illite clay.

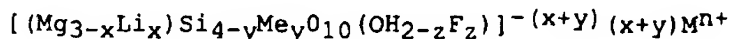
It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed such illite and kaolinite clays constitute a major component of clay soils. However, smectites, such as nontronite having an ionexchange capacity of approximately 50 meq/100 g.; saponite, which has an ion exchange capacity greater than 70 meq/100g., have been found to be useful fabric softeners.

The smectite clays commonly used for this purpose herein are all commercially available. Such clays include, for example, montmorillonite, volchonkoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "fooler clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel #1 (also, "Thixo-Jell") and Gel-white GP from Georgia Kaolin Co. Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH 450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Preferred for use herein are the montmorillonite clays.

Quite suitable are hectorites of natural origin, in the form of particles having the general formula

III



wherein Me^{III} is Al, Fe, or B; or $y=0$; M^{n+} is a monovalent ($n=1$) or divalent ($n=2$) metal ion, for example selected from Na, K, Mg, Ca, Sr.

In the above formula, the value of $(x+y)$ is the layer charge of the hectorite clay.

Such hectorite clays are preferably selected on the basis of their layer charge properties, i.e. at least 50% is in the range of from 0.23 to 0.31.

More suitable are hectorite clays of natural origin having a layer charge distribution such that at least 65% is in the range of from 0.23 to 0.31.

The hectorite clays suitable in the present composition should preferably be sodium clays, for better softening activity.

Sodium clays are either naturally occurring, or are naturally-occurring calcium-clays which have been treated so as to convert them to sodium-clays. If calcium-clays are used in the present compositions, a salt of sodium can be added to the compositions in order to convert the calcium clay to a sodium clay. Preferably, such a salt is sodium carbonate, typically added at levels of up to 5% of the total amount of clay.

Examples of hectorite clays suitable for the present compositions include Bentone EW and Macaloid, from NL Chemicals, N.J., U.S.A., and hectorites from Industrial Mineral Ventures.

Clay-flocculating agents

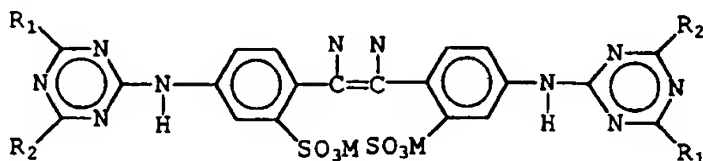
The clay softening system herein can comprise clay-flocculating agents. The compositions herein may comprise, from 0.05% to 20% by weight of the clay, of flocculating agent, if its molecular weight is 150,000-800,000 and from 0.005% to 2%, by weight of the clay, if its molecular weight is from 800,000 to 5 million. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. For proper interaction with the clay particles, the polymers should be fairly long chain, i.e., have a weight average molecular weight of at least 100,000. For sufficient water-solubility the weight average molecular weight of the polymers should not exceed 10 million. Most preferred are polymers having a weight average molecular weight of from 150,000 to 5 million.

Brighteners**Optical Brightener**

The detergent compositions herein also essentially contain from about 0.005% to 5% by weight of a certain type of hydrophilic optical brightener. Preferably the compositions herein will comprise from about 0.01% to 1% by weight of this optical brightener.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is anilino, R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-M-methylamino and M is a salt-forming cation such as sodium or potassium.

When in the above formula R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis [(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis [(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

DETERGENT ADJUNCTS

In another embodiment of the present invention, the liquid detergent composition may comprise one or more of a surfactant selected from a wide range of surfactants.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

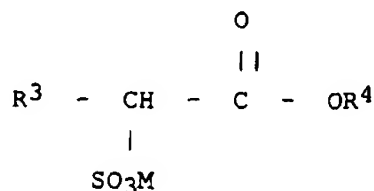
Highly preferred anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{18} alkyl component, more preferably a C_{12} - C_{15} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. monoethanolamine, methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Branched alkylsulfates are especially preferred.

Preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, more preferably C_{12} - C_{15} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted ammonium cation (e.g. monoethanolamine, methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{15} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{15}E(1.0)M$), C_{12} - C_{15} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{15}E(2.25)M$), C_{12} - C_{15} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{15}E(3.0)M$), and C_{12} - C_{15} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{15}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Other suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8 - C_{20}

carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :

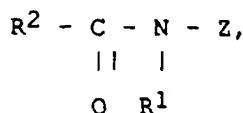


wherein R^3 is a C_8 - C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1 - C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, triethanolamine. Preferably, R^3 is C_{10} - C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10} - C_{16} alkyl.

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9 - C_{20} linear alkylbenzenesulfonates, C_8 - C_{22} primary or secondary alkanesulfonates, C_8 - C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8 - C_{24} alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12} - C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6 - C_{12} diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{-CH}_2\text{COO-M}^+$ wherein R is a C_8 - C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

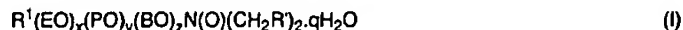
When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 5% to about 25% by weight of such anionic surfactants.

Highly preferred nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Other suitable nonionics are amine oxide surfactants. The compositions of the present invention may comprise amine oxide in accordance with the general formula I:



In general, it can be seen that the structure (I) provides one long-chain moiety $\text{R}^1(\text{EO})_x(\text{PO})_y(\text{BO})_z$ and two short chain moieties, $\text{CH}_2\text{R}'$. R' is preferably selected from hydrogen, methyl and $-\text{CH}_2\text{OH}$. In general R^1 is a primary or

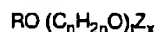
branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12} - C_{24} . The general formula also encompasses amine oxides wherein $x+y+z = 0$, $R_1 = C_8-C_{18}$, $R^2 = H$ and $q = 0-2$, preferably 2. These amine oxides are illustrated by C12-14 alkyl dimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y+z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Preferred embodiments include dodecyl dimethylamine, tetradecyl dimethylamine oxide dihydrate, hexadecyl dimethylamine oxide dihydrate and octadecyl dimethylamine oxide dihydrate.

Whereas in certain of the preferred embodiments $R^1 = H$, there is some latitude with respect to having R^1 slightly larger than H. Specifically, the invention further encompasses embodiments wherein $R^1 = CH_2OH$, such as hexadecyl-bis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearyl bis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide, dodecyl dimethyl(2-hydroxyethyl)amine oxide dihydrate.

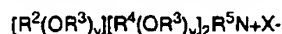
Other suitable nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

When included therein, the laundry detergent compositions of the present invention typically comprise nonionic surfactants in the weight ratio of anionic surfactant to nonionic surfactant from 6:1 to 1:3, preferably from 5:1 to 2:1.

Cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyl dimethyl ammonium halogenides, and those surfactants having the formula :



wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOH-COR^6-CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R_1 is C_8 - C_{15} alkyl, each of R_2 , R_3 and R_4 is independently C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 1 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl.

The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2 , R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
octyl or decyl triethyl ammonium chloride;
octyl or decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;

coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 lauryl dimethyl benzyl ammonium chloride or bromide;
 lauryl dimethyl (ethenoxy) ammonium chloride or bromide; choline esters (compounds of formula (i) wherein R_1 is
 $-CH_2-O-C(O)-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.5% to about 5%, preferably from about 1% to about 3% by weight of such cationic surfactants.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula $R-CH(COOH)CH_2(COOH)$ wherein R is C10-20 alkyl or alkenyl, preferably C12-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Another preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other detergent ingredients that can be included are detergent enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase, Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application Serial No. 87303761.8. Amylases include, for example, α -amylases obtained from a special strain of *B. licheniformis*, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl (Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800, and cellulases produced by a fungus of *Bacillus* N or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula* Solander).

Other suitable cellulases are cellulases originated from *Humicola Insulens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Such cellulase are described in Copending European patent application No. 93200811.3, filed March 19, 1993.

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 91202879.2, filed November 6, 1991 Carezyme (Novo).

In general, cellulases are preferred enzymes in that cellulases achieve a multicycle softening benefit, which is restricted to cotton containing fibers, by cleaving and assisting the removal of cellulosic fibrils. These normally form on the fibers during the normal washing process, and increase after consecutive washes and upon ageing of the fabric. The interaction of these fibrils with each other impart a degree of rigidity to the fabric surface that is felt by the consumer as harshness, which is alleviated by the use of cellulase enzymes.

The cellulases can be added in combination with softening silicones. Softening silicones deliver their single cycle softening benefit by depositing directly on the fabric.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P".

Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine, diisopropanolamine, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5. Non-boric acid and borate stabilizers are preferred. Borate may be conveniently incorporated into Heavy Duty Liquid detergent in the form of a solution. Boric acid has a solubility in water of about 13% at 60°C. Sodium metaborate is commercially available as a solution with activity of 10.1% (expressed in terms of B₂O₃) at 20°C.

For compact liquids it is preferred that the solution be concentrated. More concentrated solutions may be obtained by neutralising boric acid with organic amines, such as monoethanolamine (MEA).

A highly preferred concentrated borate solution can be prepared by heat treatment of aqueous borate solution. A solution heated to a temperature above 60°C, and preferably above 90°C, and maintained at that temperature for at least 5 minutes, preferably between 30 and 60 minutes will be stable at 20°C for at least a month. Using this heat treatment method, a solution with activity of at least 33% (expressed in terms of B₂O₃) can be made and stored without separation or precipitation.

Whilst various counterions may be used in the solution, e.g. sodium, potassium, MEA, triethanolamine etc, sodium is most preferred. The preferred molar ratio of Na₂O : B₂O₃ is 0.15:1 to 0.38:1, more preferably 0.22:1 to 0.35:1.

Boric acid, metaborate or borax may all be used as raw materials. Other polyols such as glycerol may also be incorporated into the concentrated solution.

Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application N 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartolotta et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 Novem-

ber, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil[®].

Other preferred suds controlling agents are described in EP 495 345. These suds controlling agents comprise a silicone antifoam compound, a carrier material and an organic coating material further containing glycerol at a weight ratio with the silicone-antifoam compound of 1:2 to 3:1.

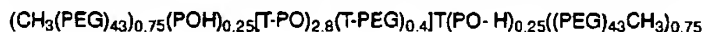
The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Other components used in detergent compositions may be employed, such as soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and non-encapsulated and encapsulated perfumes.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane 1-2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfoisobenzoid acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

The detergent compositions according to the invention can be in liquid, paste, gels, bars or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95°C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products.

Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

EXAMPLE I (A/B/C/D/E)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

| % by weight of the total detergent composition | | | | | |
|--|-----------|-------|-------|-------|-------|
| | A | B | C | D | E |
| Linear alkyl benzene sulphonate | 11.40 | - | - | - | 5 |
| Polyhydroxy fatty acid amide | - | 10 | - | 5 | 5 |
| Alkyl alkoxyfated sulfate | - | - | 9 | 9 | 9 |
| Tallow alkyl sulphate | 1.80 | 1.80 | 1.80 | 4 | 4 |
| C45 alkyl sulphate | 3.00 | 3.00 | 3.00 | - | - |
| Dispersant | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |
| Silicone fluid | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 |
| Trisodium citrate | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 |
| Citric acid | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Zeolite | 32.50 | 32.50 | 32.50 | 32.50 | 32.50 |
| Maleic acid acrylic acid copolymer | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Carezyme | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Alkalase/BAN | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 |
| Lipolase 50KLU/g | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 |
| Savinase | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sodium silicate | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Sodium sulphate | 3.50 | 3.50 | 3.50 | 3.50 | 3.50 |
| Clay | 4 | 4 | 4 | 4 | 4 |
| Polyethylene oxide | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Tinopal UNPA-GX | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Foam control agent (*) | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Minors | Up to 100 | | | | |

(*) Suds suppressor : agglomerate comprising 11% by weight of the component of polydimethylsiloxane, 14% Tallow alcohol ethoxylated, 5% of C12-C22 hydrogenated fatty acids and 70% starch.

The above compositions (Example I (A/B/C/D/E)) were very good at displaying excellent softening and dye transfer inhibiting performance.

EXAMPLE II (A/B/C/D)

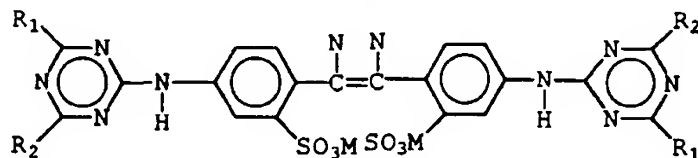
A stable liquid detergent composition according to the present invention is prepared, having the following compositions :

| % by weight of the total detergent composition | | | | |
|--|-----------|------|------|------|
| | A | B | C | D |
| Linear alkylbenzene sulfonate | 10 | 15 | 23 | - |
| Polyhydroxy fatty acid amide | - | 5 | - | 4 |
| Alkyl alkoxyated sulfate | - | - | - | 3 |
| Alkyl sulphate | 2 | 2 | 4 | 13 |
| C12-C14 dimethyl ammonium chloride | 2 | 2 | 2 | 2 |
| Fatty acid | 8 | 8 | 10 | 17 |
| Oleic acid | 2 | 2 | 2 | - |
| Citric acid | 2 | 1 | 1 | 1 |
| Diethylenetriamine pentamethylene | 1.5 | 1.5 | 1.5 | 1.5 |
| Phosphonic acid NaOH | 5 | 7 | 8 | 7 |
| Propanediol | 4 | 4 | 4 | 7 |
| Ethanol | 7 | 7 | 10 | 3 |
| Ethoxylated tetraethylene pentamine | 0.7 | 0.7 | 0.7 | 0.7 |
| Thermamyl R 300 KNU/g | 0.1 | 0.1 | 0.1 | 0.1 |
| Carezyme R 5000 CEVU/g | 0.02 | 0.02 | 0.02 | 0.02 |
| Protease 40 mg/g | 0.6 | 0.6 | 0.6 | 0.6 |
| Lipolase R 100 KLU/g | 0.1 | 0.1 | 0.1 | 0.1 |
| Endoglucanase A 5000 CEVU/g | 0.5 | 0.5 | 0.5 | 0.5 |
| Suds suppressor (ISOFOL [®]) | 2.5 | 2.5 | 2.5 | 2.5 |
| Clay | 4 | 4 | 4 | 4 |
| Tinopal-UNPA-GX | 0.2- | 0.2 | 0.2 | 0.2 |
| Minors | up to 100 | | | |

The above compositions (Example II (A/B/C/D)) were very good at displaying excellent softening and brightener performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

Claims

1. A detergent composition comprising a clay softening system characterised in that said composition further comprises a hydrophilic brightener having the structural formula



wherein R_1 is anilino, R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-M-methylamino and M is a salt-forming cation such as sodium or potassium.

2. A detergent composition according to claim 1 wherein said brightener is 4,4'-bis [(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt.
3. A detergent composition according to claim 1 wherein said brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt.
4. A detergent composition according to claims 1-3 wherein said clay softening system is a smectite type of clay.
5. A detergent composition according to claims 1-4 which is in the form of a liquid, granular, paste, bar or gel.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 1943

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claims | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X | WO-A-95 13354 (PROCTER & GAMBLE CO.) * page 8, line 9 - line 36 * * page 9, line 27 * --- | 1-5 | C1103/12 C1103/42 |
| A | EP-A-0 297 673 (THE PROCTER & GAMBLE CO.) * page 8; examples * --- | 1,4,5 | |
| A | GB-A-2 223 028 (UNILEVER PLC) * page 3, line 25 * * page 5; examples * * claims * --- | 1,4,5 | |
| A | GB-A-2 168 717 (COLGATE PALMOLIVE CO) * page 4; example 1 * --- | 1,4,5 | |
| A | WO-A-89 08695 (NOVO INDUSTRI A/S) * claims 1,10,12 * ----- | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | C110 |
| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 19 December 1995 | Examiner Pelli Wablat, B |
| CATEGORY OF CITED DOCUMENTS | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : oral-written disclosure P : intermediate document | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : oral-written disclosure P : intermediate document | | A : number of the same patent family, corresponding document | |

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172

173